Supporting Information for

$\begin{array}{l} Hydration-switchable \ charge \ transfer \ in \ the \ first \ bimetallic \\ assembly \ based \ on \ \left[Ni(cyclam)\right]^{3+} - \ magnetic \ CN-bridged \ chain \\ \left\{(H_3O)[Ni^{III}(cyclam)][Fe^{II}(CN)_6]\cdot 5H_2O\}_n \end{array}$

Beata Nowicka,^{*a} Mateusz Reczyński,^a Michał Rams,^b Wojciech Nitek,^a Jan Żukrowski,^c Czesław Kapusta^c and Barbara Sieklucka^a

 ^aFaculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland
 ^bInstitute of Physics, Jagiellonian University, Łojasiewicza 11, 30-348 Kraków, Poland
 ^cAGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Mickiewicza 30, 30-059 Kraków, Poland

1.	Experimental details and structure data for 1 (Table S1)	S2 – S4
2.	Relative redox potentials of $[Fe(CN)_6]^{3-4-}$ and $[Ni(cyclam)]^{2+/3+}$ as a function of pH in	S5
	aqueous solution (Figure S1)	
3.	Synthetic routes to compound 1 (Fig. S2)	S5
4.	Mixture of crystalline products obtained with method b (Fig. S3)	S6
5.	Fragment of the structure of 1 with atom numbering (Fig. S4)	S6
6.	Fragment of the structure of 1: spatial arrangement (Fig. S5)	S7
7.	Hydrogen bonds in the structure of 1 (Fig. S6)	S7
8.	Thermogravimetric analysis of 1 (Fig. S7)	S8
9.	ZFC/FC curves for 1, 1d and 1dhd (Fig. S8) and their description	S8 - S9
11.	Magnetization vs. field dependence at 2 K for 1 and 1d (Fig. S9)	S9
12.	Mössbauer spectra for 1 and 1d (Fig.S10)	S10
13.	Mössbauer parameters at various temperatures for 1 and 1d (Table S2)	S10
14.	Diffuse reflectance spectra of 1, 1d, 1dh and 1dhd in visible light (Fig. S11)	S11
15.	IR spectra of 1 and 1d in the CN stretching region (Fig. S12)	S11
16.	PXRD patterns for 1: measured and calculated from a single-crystal XRD structure	S12
	(Fig. S13)	

Experimental details

Syntheses

[Ni^{II}(cyclam)(NO₃)₂] i [Ni^{III}(cyclam)(NO₃)₂]NO₃ were obtained by literature methods.¹ Other reagents and solvents were commercially available and used as supplied.

$\{(H_3O)[Ni^{III}(cyclam)][Fe^{II}(CN)_6]\cdot 5H_2O\}_n (1)$

Different synthetic routes leading to compound **1** are presented in Figure S1.

Method a. Solutions of $[Ni^{III}(cyclam)(NO_3)_2]NO_3$ (44.5 mg; 0.100 mmol) and $K_4[Fe^{II}(CN)_6]\cdot 3H_2O$ (42.2 mg; 0.100 mmol) in H₂O-EtOH-MeCN (5:5:1, 25 ml) acidified with HCl (0.9 ml; 36%) were mixed together. The resulting dark blue precipitate was centrifuged and washed with a solution analogical to the mother liquor. Structure was confirmed by PXRD (Fig. S13). Found: C: 33.79; H: 6.39; N: 24.70; Calc. for $C_{16}H_{36}N_{10}O_{5.5}FeNi$: C: 33.65; H: 6.35; N: 24.53.

X-ray quality crystals were grown by slow diffusion in solvent gradient: $[Ni^{III}(cyclam)(NO_3)_2]NO_3$ (44.5 mg; 0.100 mmol) was dissolved in 25 ml of H₂O-EtOH-MeCN (3:6:1) mixture acidified with conc. HCl (0.9 ml; 36%). This solution was layered in test tubes over the solution containing K₄[Fe^{II}(CN)₆]·3H₂O (42.2 mg; 0.100 mmol) and HCl (0.9 ml; 36%) in H₂O-EtOH-MeCN (6:3:1 25 ml), with a buffer layer containing HCl (0.9 ml; 36%) in H₂O-EtOH-MeCN (5:5:1, 25 ml). After two weeks dark blue needle-shaped crystals of **1** were formed together with small quantities of [Ni(cyclam)]₃[Fe(CN)₆]₂·22.5H₂O.² The impurity was removed by sieving and washing with the buffer solution.

Method b: $[Ni^{II}(cyclam)(NO_3)_2]$ (38.3 mg; 0.100 mmol) was dissolved in 25 ml of H₂O-EtOH-MeCN (3:6:1) mixture acidified with conc. HCl (0.9 ml; 36%). This solution was layered in test tubes over the solution containing K₃[Fe^{III}(CN)₆] (32.9 mg; 0.100 mmol) and HCl (0.9 ml; 36%) in H₂O-EtOH-MeCN (6:3:1 25 ml), with the buffer layer containing HCl (0.9 ml; 36%) in H₂O-EtOH-MeCN (5:5:1, 25 ml). After 2 weeks a mixture of crystals (Fig. S3) was obtained. The main product **1** in the form of dark blue needles was isolated by sieving and washing with the buffer solution.

Method c. Solution of $K_3[Fe^{III}(CN)_6]$ (329.0 mg; 1.000 mmol; 20 ml H₂O) was added dropwise to hot water solution of $[Ni^{II}(cyclam)(NO_3)_2]$ (19.2 mg; 0.050 mmol, 10 ml) with constant stirring. The initial brown precipitate of $[Ni(cyclam)]_3[Fe(CN)_6]_2 \cdot 22.5H_2O_2^2$ gradually dissolved. The resulting solution was cooled and HCl was added (0.35 ml 36%). Within a minute the dark blue precipitate of **1** was formed, together with a small amount of light brown crystals of $[Fe^{III}(cyclam)][Fe^{III}(CN)_6] \cdot 6H_2O_2^3$

Structure determination

Diffraction data for compound **1** were collected on a single crystal sealed in a capillary under the solvent mixture analogical to the mother liquor at room temperature using the Nonius KappaCCD four circle diffractometer equipped with the Mo (0.71069 Å) K α radiation source and graphite monochromator. The structure was solved by direct methods using SIR-97⁴ the refinement and further calculations were carried out using SHELXL-97.⁵ All non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares on F². H atom were located from the difference Fourier map and refined isotropically.

fo	rmula	$C_{16}H_{37}FeN_{10}NiO_6$		
formula v	weight (g/mol)	579.80		
	T (K)	293		
	λ (Å)	0.71073		
crystal system		monoclinic		
spac	ce group	<i>C</i> 2/m		
unit cell a (Å)		13.8630(4)		
	<i>b</i> (Å)	12.5020(4)		
	<i>c</i> (Å)	10.0930(4)		
	β (°)	133.020(2)		
V	√(Å ³)	1278.92(8)		
Z		2		
D _x ((Mg/m³)	1.506		
absorption coefficient (mm ⁻¹)		1.35		
F(000)		608		
crystal size (mm × mm × mm)		$0.30 \times 0.05 \times 0.05$		
θ range (°)		3.3-27.5		
limiting indices		$h = -17 \rightarrow 18$		
		$k = -16 \rightarrow 16,$		
		$l = -13 \rightarrow 12$		
collecte	d reflections	5355		
symmetry—independent reflections		1530		
$R_{\rm int}$		0.052		
completeness [%]		99.4		
max and min transmission		0.678 and 0.564		
refinem	ent method	full-matrix least-squares on F ²		
data/restrains/parameters		1530/6/105		
GOF on F^2		1.04		
final R indices		$R[F^2 > 2\sigma(F^2)] = 0.032$		
		$wR(F^2) = 0.081$		

 Table S1. Crystal data, data collection and refinement details for 1.

Measurements

Elemental C, N, H analyses were performed on an ELEMENTAR Vario Micro Cube CHNS analyser. Relative Ni and Fe content was determined by microanalysis on HITACHI S-4700

SEM equipped with NORAN Vantage microanalysis system. Thermogravimetric analysis was measured on a Mettler Toledo TGA/SDTA 851e equipped with a QMS Thermostar GSD 300 T Balzers detector in a temperature range of 30-350 °C with heating rate of 2 °/min, under Ar atmosphere. Powder XRD patterns were measured at room temperature between 3 and 70° 2 θ angle on a PANalytical X'Pert PRO MPD diffractometer with a capillary spinning add-on using CuK α radiation ($\lambda = 1.54187$ Å). Samples in form of dry powder or thick suspensions were sealed in 0.7 mm glass capillaries. The reference powder patterns were generated using Mercury 3.3 software.⁶ Magnetic measurements were performed using a Quantum Design MPMS-3 EVERCOOL magnetometer on samples sealed in polyethylene bags. The diamagnetic correction for sample holders was estimated and subtracted. Moessbauer ⁵⁷Fe spectra at 300, 80 and 4.2 K were measured on a self-made apparatus at the AGH University of Science and Technology, Department of Solid State Physics. An XRF microanalysis was performed using a HITACHI S-4700 scanning electron microscope equipped with a NORAN Vantage microanalysis system. Diffuse reflectance spectra in 200-1100 nm range were measured on a Perkin Elmer Lambda 35 spectrophotometer with an integrating sphere. IR spectra in 4000–500 cm⁻¹ range were measured on a Thermo Scientific Nicolet iS5 spectrometer with iD5 ATR-Diamond add-on. Cyclic voltammetry measurements were performed on an mtm-anko M161C electrochemical analyser in a three-electrode setting with Pt working electrode against silver chloride reference electrode in a 100-1100 mV range at a 25 mV/s sweeping rate for 0.05 M solutions in 0.1 M KCl, with pH adjusted by addition of conc. HCl.

References

- 1. D. E. Berry, S. Girard and A. McAuley, J. Chem. Edu., 1996, 73, 551-554.
- E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekas, F. Lloret, J. M. Morenoa and H. Stoeckli-Evans, *Chem. Commun.*, 1999, 987–988.
- E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekas, M. Klinga and J. M. Moreno, *Chem. Commun.*, 1998, 1071–1072.
- 4. A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
- 5. G. M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64, 112.
- C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, J. Appl. Crystallogr., 2006, 39, 453–457.



Fig. S1. Relative redox potentials of $[Fe(CN)_6]^{3-/4-}$ and $[Ni(cyclam)]^{2+/3+}$ as a function of pH in aqueous solution.



Fig. S2. Synthetic routes to compound **1**. In structure fragments: Fe - red balls, Ni - green balls, C - grey sticks, N - blue sticks; hydrogen atoms and water molecules omitted for clarity



Fig. S3. Mixture of crystalline products obtained in the reaction between $[Ni(cyclam)]^{2+}$ and $[Fe(CN)_6]^{3-}$ in acidified solution with HCl: brown plates: $\{[Ni(cyclam)]_3[Fe(CN)_6]_2 \cdot 22.5H_2O\}_n^2$ light brown blocks: $\{[Fe(cyclam)][Fe(CN)_6] \cdot 6H_2O\}_n^3$ dark blue needles: $\{(H_3O)[Ni(cyclam)][Fe(CN)_6] \cdot 5H_2O\}_n$ (1).



Fig. S4. Fragment of the structure of 1 with atom numbering. Thermal ellipsoids at 50% probability.



Fig. S5. Structure of **1**: a) view along b axis; b) view along the chains in [1 0 -1] direction. Colours: Ni-green, Fe-orange, N-blue, C-grey, O-red, H-white.



Fig. S6. Hydrogen bonds in the structure of 1.



Fig. S7. Thermogravimetric analysis of 1 with QMS detection.



Fig. S8. Zero-field cooling and field cooling magnetization for **1** and **1d** (left) and for **1dhd** (right).

Description of ZFC/FC measurements results

The sharp increase of FC magnetization at 5.5 K (Fig S8, left) is most probably related to the ordering of the **1d** phase, because it is not present in the paramagnetic hydrated phase **1**. The ZFC curve for **1d** goes negative below 5 K, because the sample was cooled in a slightly negative field. The same feature is also present as a small remnant magnetization of 0.03 μ B in *M*(*H*) measurement at 1.8 K (Fig. S9). Such magnetization may appear due to numerous defects in Fe-Ni spin structure produced by disorder of the oxidation states of the ions. Even if

an AF ordering between the chains is anticipated from M(H) measurement at 1.8 K, the locally non-compensated magnetic moments can produce such difference in ZFC/FC curves. For sample **1dhd** the measurements (Fig S8, right) were performed in the field of 200 Oe in order to allow direct comparison with the data presented in ref. 8 (*Curr. Appl. Phys.*, 2011, **11**, 271). Below 6K the curves are similar to those of the sample **1d**. However, at higher temperatures additional characteristic features appear, which are related to the formation of another phase during rehydration process. The comparison of ZFC/FC curves in the range from 10 to 30 K with ref. 8 suggests that this impurity phase is Ni-Fe PBA.



Fig. S9. Magnetization vs. field dependence at 2 K for 1 and 1d.



Fig. S10. Mössbauer spectra for 1 (a) and 1d (b).

Sample	<i>T</i> (K)	δ^{a} (mm/s)	⊿ (mm/s)	Γ (mm/s)	A (%)	Assignment		
	300	-0.11	0.14	0.13	100	LS Fe(II)		
1	80	-0.021	0.14	0.13	100	LS Fe(II)		
	4.2	-0.02	0,14	0.13	100	LS Fe(II)		
	300 80	-0.18	1.07	0.28(2)	19	LS Fe(III)		
		-0.14	0.58(2)	0.28(2)	16	LS Fe(III)		
		-0.11	0.11	0.14	65	LS Fe(II)		
		-0.08	1.20	0.24	28	LS Fe(III)		
1d		-0.04	0.83	0.24	13	LS Fe(III)		
		-0.04	0.10	0.16	59	LS Fe(II)		
		-0.07	1.24	0.28	20	LS Fe(III)		
	4.2	-0.03	0.90	0.28	18	LS Fe(III)		
		-0.03	0.09	0.15	62	LS Fe(II)		
^a The value of δ is reported relative to metallic Fe; LS: low spin.								
Fitting error in δ , Δ and Γ , if not mentioned, remains below 0.01 mm/s.								

Table S2. Mössbauer parameters at various temperatures for 1 and 1d.



Fig. S11. Diffuse reflectance spectra of 1, 1d, 1dh and 1dhd in visible light.



Fig. S12. IR spectra of 1 and 1d in the CN stretching region.



Fig. S13. PXRD pattern for sample of **1** obtained by quick precipitation (top) in comparison to the pattern calculated from single-crystal XRD structure determination (bottom).